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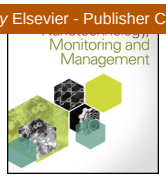

River pollution: Assessment of hydro-philic and phobic nature of persistent organic contaminants

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ABSTRACT

Natural purification of persistent organics by sorption during riverbank filtration (RBF) depends on their hydrophilic or hydrophobic nature. It can be ascertained by octanol/water partition coefficient (K_{OW}) and specific ultra violet absorbance (SUVA). This motivated the authors to analyze K_{OW} and SUVA, firstly, of some mixed synthetic samples of organics and secondly, of polluted water samples from the River Hindon. Monthly water samples of the Hindon were collected from five locations (latitude 28°38′08.64″ to 29°36′42.55″N and longitude 77°23′38.27″ to 77°34′19.38″E) and were analyzed for cumulative water-quality parameters total organic carbon (TOC), UV-A, biochemical oxygen demand (BOD) and chemical oxygen demand (COD). The low ratio of BOD_5-COD (~0.13) is indicative of persistent nature of organics in the river water. Organics in the water samples were also analyzed by GC–MS and their log K_{OW} values were obtained from the literature ranged from −0.84 to 2.15. Log K_{OW} values of the water samples from four locations were between 0.11 and 0.37 but were around −0.43 at the fifth locations. Similarly, SUVA values of water from the same four locations were between 0.64 and 0.80 whereas the SUVA of the fifth water sample varied from 0.49 to 0.59. Both SUVA and K_{OW} values reveal hydrophilic nature of the Hindon water samples.

Capsule

Characterization of synthetic aqueous samples containing the mixture of organics and river water samples by K_{OW} and SUVA.

1. Introduction

There is an emerging concern about the presence of persistent organics in rivers, lakes and ground waters. These organic impurities are generally assessed by collective parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD) and total organic carbon (TOC). The ratio of BOD–COD indicates biodegradable nature of aqueous organic impurities and correlation between TOC and COD suggests the oxidation state of carbon present in the organics. Rivers, which receive aerobically treated effluents, are polluted with organics of (i) low biodegradability (BOD/COD <0.35; Mohan et al., 2005) and (ii) carbon in higher oxidation state (>+2). Examples of oxidation state of carbon for some organic compounds are hexachloroethane-(+3), chloroform-(+2), carbon tetrachloride-(+4), formic acid-(+2), phosphoric acid-(+3), etc. In other words these pollutants can be defined as stable or persistent organics. Piet and Zoeteman (1980) and Sontheimer (1988) have reported the presence of persistent organic contaminants such as detergents, disinfection by-products, food processing wastes, insecticides, herbicides, petroleum hydrocarbons, volatile organic compounds (VOCs), personal care products, pharmaceuticals etc. in trace amount in surface waters. These contaminants which may enter in to natural water resources from point and non-point sources are of concern as they can directly or indirectly affect human health. Most of these organics are removed by sorption or advanced oxidation. Removal by sorption depends on the hydrophobic nature of aqueous organics, which can be assessed by octanol water partition coefficient (K_{OW}) and specific ultra violet absorbance (SUVA). K_{OW} is a parameter that has been correlated to the ratio of BOD/COD, water solubility (Miller, 1985), organic carbon–water partition coefficient (K_{OC}) and retardation factor (R_f) (Karickhoff, 1981; Chiou et al., 1982; Kanazwa, 1989). K_{OW} is determined by partitioning the organics between octanol as an immiscible liquid (the hydrophobic phase) and water (the hydrophilic phase) (Pezzagno et al., 1985). The hydrophobic nature increases with increase in K_{OW}. The logarithm value

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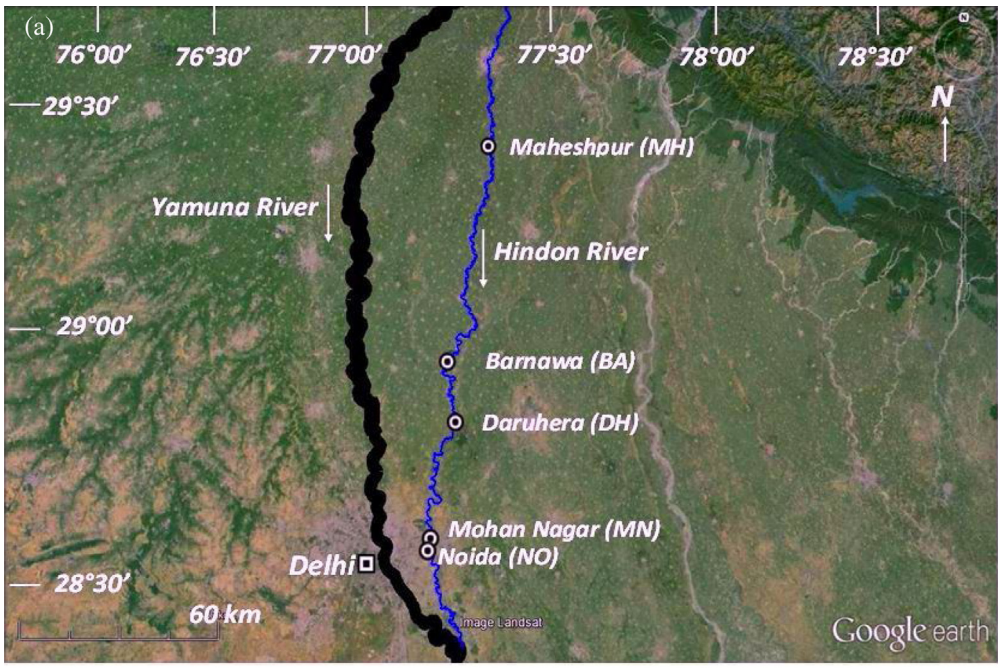

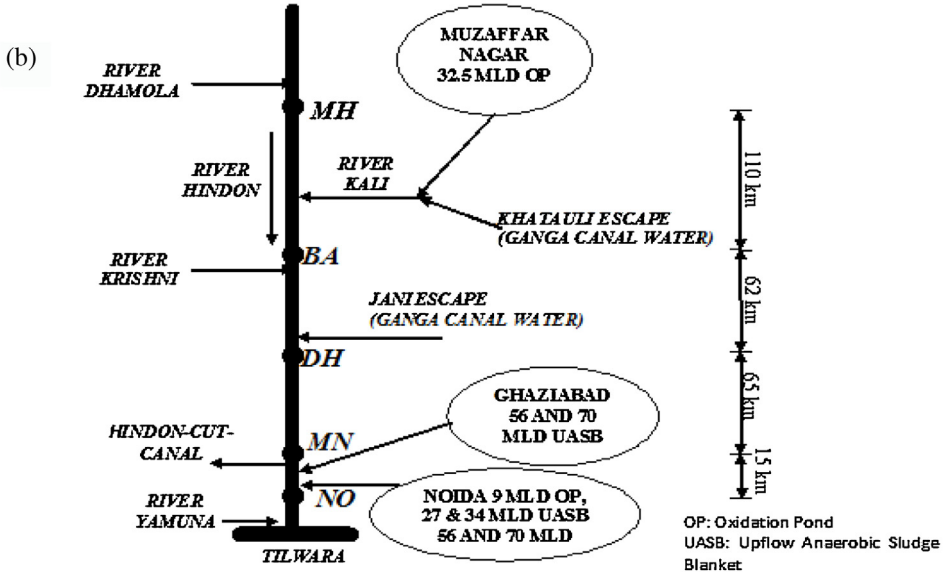

Fig. 1. (a) Map and (b) Schematic diagram of the River Hindon showing five sampling locations ( ), tributaries/water additions and abstractions.

of octanol/water partition coefficient ($\log K_{OW}$) < 1 is indicative of hydrophilic nature, 1 < $\log K_{OW}$ < 2, moderately hydrophobic and >2 strongly hydrophobic nature of organics in water (Chiou et al., 1982 Moss et al., 2002).

Specific UV absorbance (SUVA) in (mg^{-1} m^{-1} L) represents the ratio of UV-A (m^{-1}) to DOC (mg/L) (USEPA, 2005; Karanfil et al., 2002; Li et al., 1998; Archer and Singer, 2006). Values of SUVA between 2 and 4 indicate mixture of hydrophobic and hydrophilic compounds; >4 suggest presence of hydrophobic compounds and <2 denote non humic substances of low molecular weight, preferably hydrophilic or moderately hydrophobic compounds (Archer and Singer, 2006; Chin et al., 1994; Wang et al., 1990; Hautala et al., 2000; Weishaar et al., 2003; Liu, 2010; Bazrafshan et al., 2012). Most of the aromatic compounds which are hydrophobic in nature have greater SUVA values than aliphatic compounds (hydrophilic nature).

Values of SUVA and $\log K_{OW}$, indicators of hydrophilic or hydrophobic nature of organic impurities, are important attributes for the removal of persistent organics by sorption (Ellis, 1989; Sangster, 1989; Karanfil et al., 2002). Pradhan et al. (2013) established correlation between K_{OW} and SUVA for carbohydrates, volatile fatty acids, alcohols and different aromatic compounds. This study also emphasized that SUVA at λ_{max} was a better indicator of the nature of organics than SUVA at 254 nm.

K_{OW} for individual compounds is documented (Sangster, 1989; Hansch and Leo, 1979; Eadsforth and Moser, 1983). However, K_{OW} of polluted water, which contains variety of pollutants, has not been reported. Therefore, to understand the partitioning of mixture of organics, a few synthetic samples of known composition containing mixture of two or three organic compounds as well as polluted water samples from the River Hindon were analyzed for K_{OW} and SUVA.

Table 1
Description of sampling locations of River Hindon.

Locations	Latitude, longitude	Inflows and outflows before a particular sampling location
MH (Maheshpur)	29°36′42.55″N, 77°34′19.38″E	Treated and untreated sewage from Saharanpur through River Dhamola and effluents from industries like pulp and paper, distillery, etc.
BA (Barnawa)	29°06′49.72″N, 77°26′28.20″E	Sewage from Muzaffarnagar through River Kali, discharges from industries like sugar, distillery, etc. and fresh Ganga Canal water through Khatauli Escape and River Kali
DH (Daruhera)	28°57′30.10″N, 77°28′16.13″E	Fresh Ganga Canal water through Jani Escape
MN (Mohan Nagar)	28°39′58.95″N, 77°24′03.55″E	Sewage and industrial effluents from Ghaziabad
NO (Noida)	28°38′08.64″N, 77°23′38.27″E	Treated and untreated municipal effluents from Ghaziabad and Noida, abstraction of water via Hindon Cut Canal

Table 2
K_{OW} and SUVA of organics used for synthetic samples (Pradhan et al., 2013).

Compounds	Glucose	Glutamic acid	Fructose	Methanol	Acetone	Benzene	Nitrobenzene	KHP
K_{OW}	5.1×10^{-4}	15×10^{-4}	38×10^{-3}	0.17	0.76	107	63.1	25.1
$SUVA_{\lambda max}$	0.0033	0.001	0.223	0.305	0.43	1.13	0.95	0.73
$K_{OW}/SUVA_{\lambda max}$	0.15	1.5	0.17	0.55	1.76	94.7	66.4	34.4
$\log K_{OW}/SUVA_{\lambda max}$	−1000	−2820	−5.38	−2.52	−0.28	1.8	1.89	1.91

2. Materials and methods

2.1. Preparation of synthetic samples

Synthetic samples, 21 in number, were prepared from eight organic compounds namely glucose, benzene, glutamic acid, fructose, methanol, acetone, potassium hydrogen phthalate (KHP) and nitrobenzene. The K_{OW} and SUVA of these organics represent a wide range of variation (Table 2; Pradhan et al., 2013). An aqueous sample containing mixture of organics, the concentration of each organic may affect partitioning, therefore values of K_{OW} and SUVA of samples containing same organics in three different ratios were determined at octanol to water ratio of 1:1, 1:2 and 2:1. Details pertaining to the composition of synthetic samples are given in Table 3. The two solvents i.e. HPLC grade n-octanol and double distilled water were pre-saturated with each other by mixing equal amounts and stirring for 24 hours.All samples were characterized by DOC and UV-A.

2.2. Natural samples

With this background, it became necessary to study a few natural samples. Water samples were collected from five sampling locations on the River Hindon once a month from August 2011 to May 2012. The river originates from the upper Shivalik hills (lower Himalayas) and mainly flows through four districts namely Saharanpur, Muzaffarnagar, Meerut and Ghaziabad in Western part of Uttar Pradesh, India and finally joins the River Yamuna downstream of Delhi at Tilwara. Sampling locations on the river Hindon are shown in Fig. 1(a). Schematic diagram of the River Hindon, tributaries/water additions, abstractions and sampling locations and distances between them are shown in Fig. 1(b). Other relevant details regarding sampling locations are tabulated in Table 1.

Water samples were preserved and transported to the Environmental Engineering Laboratory of IIT Roorkee for the analysis of water quality parameters, K_{OW} and SUVA (APHA, 2005). Temperature, pH and dissolved oxygen (DO) of the samples were measured on-site using Hach multi parameter probe HQ-40D. For DOC measurement, a part of each sample was filtered through a fiberglass filter (0.45 μm) as per the (APHA, 2005) and Huizhong et al. (2001). COD and BOD_5 of filtered and unfiltered samples were determined by closed reflux and dilution methods respectively (APHA, 2005). TOC and DOC were determined by Shimadzu-TOC-V_{CSN} analyzer. UV-A of filtered samples was measured at 254 nm by the Hach DR-5000 UV–vis Spectrophotometer with 10 mm quartz cell. Organic compounds in the Hindon water were identified by GC–MS (Varian 450-GC and 240-MS).

2.3. Measurement of K_{OW} and SUVA

K_{OW} of synthetic samples containing mixture of organics and Hindon water samples was determined by shake-flask method at 25 °C followed by OECD (1981) and as described by Pradhan et al. (2013). SUVA of corresponding samples was measured at λ_{max} and 254 nm. Hindon water samples were filtered by passing through the 0.45 μm pore size filter paper. Synthetic samples and filtered Hindon water samples were stirred gently for half an hour in conical flasks with octanol pre-saturated distilled water in the ratio of 1:1, 1:2 and 2:1. Samples were subsequently centrifuged and separated into octanol and water phases in a separatory funnel. Volume of octanol and sample were recorded to apply volume correction. Concentration of the contaminants in water phase was measured by DOC and corresponding UV-A was also measured at λ_{max} and 254 nm. The presaturated distilled water was considered as blank solution. Maximum Wavelength of each sample was determined by scanning wavelength from 200 to 400 nm. According to APHA (2005) wavelength at 254 nm is the standard wavelength for the detection of organic matter in natural water sample. Concentration of the contaminants in octanol was estimated by taking the difference between the initial and residual water concentrations after equilibrating sample with octanol. Values of DOC and UV-A were corrected for residual octanol in the aqueous phase. The K_{OW} was measured at three different ratios of octanol and water. The K_{OW} and SUVA values were verified by statistical analysis.

3. Results and discussion

3.1. K_{OW} and SUVA of synthetic samples containing mixture of organic compounds.

K_{OW} and SUVA at λ_{max} and 254 nm of synthetic samples containing single organics are reported in Table 2a K_{OW} of natural samples containing mixture of wide range of aliphatic and aromatic compounds is likely to be sensitive to the ratio of octanol to water used for partitioning. To asses this, K_{OW} and SUVA of synthetic samples

Table 3
Average values of K_{OW} and SUVA of synthetic samples.

Concentration, g/L			DOC (mg/L)	UV-A (cm^{-1})		Mean value ± SD: (SE)				Mean [K_{OW}/$SUVA_{\lambda max}$ ($mg\,m\,L^{-1}$)]	Mean [log K_{OW}/$SUVA_{\lambda max}$ ($mg\,m\,L^{-1}$)]
						$SUVA_{\lambda max}$ ($mg\,m\,L^{-1}$)		K_{OW}	Log K_{OW}		
1. Glucose and benzene, λ_{max} = 268 nm; *R* is regression coefficient											
Glucose	Benzene			R^2 = 0.962	R^2 = 0.957	λ_{max}	254 nm				
			λ_{max}	254 nm							
1.5	1.5		1978	4.771	2.136	0.223 ± 0.03: (0.034)	0.094 ± 0.01: (0.008)	1.85 ± 0.05: (0.047)	0.26 ± 0.01: (0.011)	8.29	1.16
1.5	2		2438	6.216	2.462						
2	1.5		2175	5.046	2.079						
2. Glucose and glutamic acid, λ_{max} = 235 nm											
Glucose	Glutamic acid			R^2 = 0.851	R^2 = 0.70						
2	2		1609	1. 045	0.37	0.073 ± 0.01: (0.001)	0.03 ± 0.01: (0.002)	0.54 ± 0.04: (0.013)	−0.26 ± 0.03: (0.01)	8.43	−4.06
2	1		1203	0.89	0.204						
1	2		1207	0.953	0.554						
3. Benzene and potassium hydrogen phthalate (KHP), λ_{max} = 280 nm											
Benzene	KHP			R^2 = 0.980	R^2 = 0.962						
0.5	0.5		681.8	13.95	3.361	2.077 ± 0.05: (0.003)	0.510 ± 0.02: (0.034)	112 ± 6.4: (2.137)	2.05 ± 0.03: (0.01)	55.8	0.98
0.5	0.1		497.6	10.13	2.974						
0.1	0.5		321.6	6.602	1.585						
4. Methanol and acetone, λ_{max} = 267 nm											
Methanol	Acetone			R^2 = 0.899	R^2 = 0.818						
2	2		1978	0.866	0.144	0.047 ± 0.01: (0.004)	0.008 ± 0.01: (0.0003)	0.85 ± 0.04: (0.012)	−0.06 ± 0.02: (0.006)	18.05	−1.27
2	1		1609	0.765	0.132						
1	2		1361	0.628	0.107						
5. Glucose, benzene and KHP, λ_{max} = 286 nm											
Glucose	Benzene	KHP		R^2 = 0.998	R^2 = 0.987						
0.2	0.2	0.2	348.5	4.043	2.547	1.083 ± 0.06: (0.018)	0.668 ± 0.09: (0.005)	27.6 ± 1.44: (0.479)	1.44 ± 0.03: (0.01)	25.4	1.33
0.5	0.2	0.1	421	4.685	3.251						
0.2	0.5	0.1	770.5	8.173	4.815						
6. Benzene, nitrobenzene and KHP, λ_{max} = 286 nm											
Benzene	Nitro-benzene	KHP		R^2 = 0.999	R^2 = 0.991						
0.2	0.2	0.2	369.4	7.621	3.424	2.131 ± 0.031: (0.034)	0.848 ± 0.081: (0.084)	339 ± 9.3: (9.343)	2.51 ± 0.70: (0.014)	135	1.17
0.1	0.2	0.3	344.8	7.413	2.861						
0.2	0.3	0.1	308.8	6.809	2.341						
7. Glucose, benzene and fructose, λ_{max} = 272 nm											
Glucose	Benzene	Fructose		R^2 = 0.986	R^2 = 0.970						
0.4	0.4	0.4	856.7	2.211	0.48	0.263 ± 0.05: (0.016)	0.060 ± 0.01: (0.004)	1.76 ± 0.05: (0.016)	0.24 ± 0.01: (0.004)	6.7	0.91
0.4	0.1	0.4	409.6	1.116	0.274						
0.1	0.4	0.1	441.3	1.345	0.314						

Table 4a
Hindon River: Statistical data of water quality parameters (Aug 201–May 2012) and two way ANOVA values.

Parameters	Range of values (mean value ± standard deviation):SE					*t-test (ANOVA)	
	MH	BA	DH	MN	NO	F-factor	*p*-values
pH	7.4–8.2 (7.7 ± 0.3):0.1	7.5–8.2 (7.9 ± 0.2):0.06	7.3–8.9 (7.9 ± 0.4):0.04	7.4–8.1 (7.8 ± 0.3):0.1	7.5–8.0 (7.7 ± 0.2):0.06	5.7	<0.05
TOC (mg/L)	87.3–217 (131.1 ± 45.4):15.2	80.5–196 (115.2 ± 8.1):12.7	45.6–144 (70.9 ± 30.7):10.2	57.4–130 (86.3 ± 21.2):7.1	65–128 (92.1 ± 17.3):5.7	42.7	<0.001
DOC (mg/L)	71.3–193 (105 ± 38.4):12.8	56.0–171 (92.2 ± 40.4):13.4	33.8–89.8 (54.5 ± 18.5):6.16	41.5–84.7 (65.1 ± 14.3):4.76	52.1–101 (73.4 ± 17.0):5.66	94.3	<0.001
$(BOD_5)_T$ (mg/L)	17.5–68.1 (33.1 ± 16):5.3	12.3–47.3 (25.1 ± 10):3.3	10.4–5.8 (15.8 ± 4.9):1.6	11.2–37.5 (18.1 ± 7.5):2.5	16.1–43.8 (23.3 ± 8.3):2.7	21.7	<0.002
$(BOD_5)_S$ (mg/L)	4.52–34 (15.8 ± 8.6): 2.8	4.01–20.8 (12.1 ± 5.8):2.0	3.8–13 (7 ± 2.8):1.0	4–11.2 (7.7 ± 2.8):1.0	4.6–16.1 (10.1 ± 4.4):1.4	9.7	<0.05
COD_T (mg/L)	75.2–450 (210 ± 114):38	54.1–591 (185 ± 157):52.3	27–130 (67 ± 29.5):9.8	47–205 (100 ± 57):19	57.3–210 (135 ± 66.2):22.0	34.5	<0.002
COD_S (mg/L)	58.4–266 (115 ± 59):19.6	42–170 (92.7 ± 42.6):14.2	21.5–98.2 (45.1 ± 23.3):7.76	28.7–86.4 (52.7 ± 15.5):5.1	36.4–113 (77.3 ± 31):10.3	21.6	<0.002
UV-$A_{\lambda max}$ (m^{-1})	51–135 (73 ± 27):9.0	39–124 (63.7 ± 27):9.0	20–68.4 (34.5 ± 15):5.0	32.4–58.2 (48.4 ± 9):3.0	38.4–74.1 (54.2 ± 1):3.6	11.6	<0.02

T: Total value (unfiltered samples), *S*: soluble value (filtered samples); λ_{max} = 254 nm; F (Fischer factor) = sum of squares between the stations/mean square error.
*(Gupta and Kapoor, 2002); *p*: probability (significant at $p < 0.05$).

Table 4b
Hindon River: K_{OW}, $SUVA_{\lambda max = 254\ nm}$ and other normalized water quality parameters (Aug 2011–May 2012) and two way ANOVA values.

Parameters	Range of values (mean value ± standard deviation):SE					*t-test (ANOVA)	
	MH	BA	DH	MN	NO	F-factor	*p*-values
$SUVA_{\lambda max}$ ($mg\ m^{-1}\ L^{-1}$)	0.64–0.72 (0.70 ± 0.02):0.01	0.65–0.8 (0.75 ± 0.05):0.02	0.49–0.59 (0.57 ± 0.03):0.01	0.66–0.8 (0.74 ± 0.05):0.02	0.64–0.8 (0.73 ± 0.05):0.02	4.6	<0.05
K_{OW}	1.47–1.59 (1.55 ± 0.03):0.01	2.15–2.32 (2.28 ± 0.05):0.02	0.34–0.38 (0.36 ± 0.01):0.003	2.02–2.08 (2.05 ± 0.02):0.01	1.86–2.12 (2.01 ± 0.08):0.03	6.2	
Log K_{OW}	0.11–0.19 (0.17 ± 0.02):0.01	0.34–0.37 (0.35 ± 0.01):0.003	(−0.40) to (−0.46) (−0.43 ± 0.02):0.01	0.30–0.32 (0.31 ± 0.01):0.003	0.26–0.32 (0.30 ± 0.02):0.01	7.4	
$K_{OW}/SUVA_{\lambda max}$ ($mg^{-1}\ m\ L$)	2.21	3.04	0.63	2.77	2.75	–	
Log K_{OW}/SUVA ($mg^{-1}\ m\ L$)	0.24	0.46	−0.75	0.41	0.41	–	
DOC/TOC	0.6–0.9 (0.8 ± 0.08):0.03	0.61–0.95 (0.78 ± 0.11):0.04	0.62–0.94 (0.79 ± 0.1):0.03	0.6–0.9 (0.76 ± 0.1):0.03	0.65–0.94 (0.8 ± 0.1):0.03	4.3	<0.5
COD_T/TOC (mmol/mmol)	0.22–1.08 (0.61 ± 0.26):0.08	0.24–1.35 (0.59 ± 0.38):0.13	0.20–0.71 (0.36–0.14):0.05	0.23–0.89 (0.44 ± 0.22):0.07	0.24–1.08 (0.57 ± 0.3):0.10	5.3	
Oxidation state	1.94–3.31 (2.56 ± 0.32)	1.49–2.92 (2.67 ± 0.43)	1.98–3.24 (2.21 ± 1.98)	2.46–3.31 (2.88 ± 0.23)	2.55–3.07 (2.87 ± 0.18)	10.1	

$\#OS = 4[1 - (\frac{COD}{TOC}) \times (\frac{12}{32})]$.

Table 5
Hindon River: Organic compounds identified by GC–MS (Aug 2011–May 2012).

Name of the compound	Molecular formula	Mol.wt. (g/mol)	[a]Log K_{OW}	Sampling locations		TOC (mg/L) (mean ± standard deviation)		
				MH(131.1 ± 45.4)	BA(115.2 ± 38.1)	DH(70.9 ± 30.7)	MN(86.3 ± 21.2)	NO(92.1 ± 17.3)
Valeric anhydride	$C_{10}H_{18}O_3$	186	2.15	√	√	√	√	√
4-Aminobenzoic acid	$C_7H_7NO_2$	137	0.68	√	√	√	√	√
2-Methylpyridine	C_6H_7N	172	0.32	√	√	–	√	√
Ethyl maleate	$C_6H_7O_4$	172	0.89	–	√	√	√	√
3-Cyclobut-1-enyl-3-hydroxy-2-methyl-propionic acid	$C_8H_{12}O_3$	156	0.59	√	–	–	√	√
2-Pyrrolidinone	C_4H_7NO	85	−0.39	√	√	√	–	–
Ethylenediamine	$C_2H_4(NH_2)_2$	61	0.19	√	√			
3-Cyclobut-1-enyl-3-hydroxy-2-methyl-propionic acid	$C_8H_{12}O_3$	156	0.59	√	√	–	–	–
Oxaldehyde	$C_2H_2O_4$	58	0.19	√	–	√	–	–
2-Hydroxyethyl acrylate	$CH_2=CHCOOCH_2CH_2OH$	116	0.54	–	√	√	–	–
Diethylenetriamine	$C_4H_{13}N_3$	103	0.29	–	–	–	√	√
Pyrrolidine, 3-methyl-	$C_5H_{11}N$	85	1.19	–	–	–	√	√
3-Amino-2-chloro-pyridine	$C_5H_5ClN_2$	128	0.04	–	–	√	–	–
3-Mercaptopropane-1,2-diol	$C_3H_8O_2S$	108	−8.40	–	–	√	–	–

[a]RSC, Advancing Chemical Science. www.chemspider.com (assessed on 8.3.13).

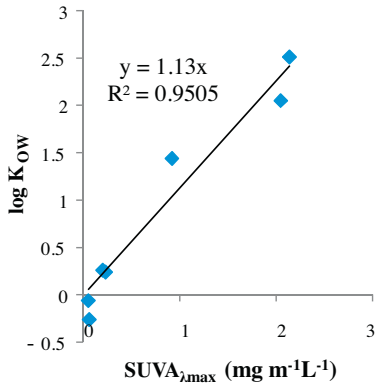

Fig. 2. Correlation between $SUVA_{max}$ and log K_{OW} of synthetic samples.

containing the mixture of two and three organics were determined at octanol to water ratio of 1:1, 1:2 and 2:1 (Table 3).

Mean of K_{OW} and SUVA at λ_{max} and 254 nm of synthetic samples are given in Table 3. Statistical analysis of the data in terms of standard deviation (SD) and standard error (SE) have also been included in Table 3. SD and SE indicate that K_{OW} and SUVA values are not sensitive to the concentration of individual organic as well as to the ratio of octanol to water used for partitioning. Further perusal of results indicates that K_{OW} and SUVA of the synthetic samples containing the mixture of organics are different from samples that contain single compound.

Following inferences are drawn on the basis of statistical analysis of data is that K_{OW} and SUVA of a sample containing mixture of organics is not affected by the (i) concentration of the individual organic in a mixture and (ii) ratio of octanol to water used for partitioning organics in two phases. Among seven samples listed in Table 3, two of the samples viz. methanol-acetone and glucose-glutamic acid do not contain any aromatic compound. $SUVA_{\lambda max}$ and K_{OW} of these samples are less than 0.1 L mg^{-1} m^{-1} and 1.0, respectively. The present observation on mixture of organic compounds is in conformity with the observations recorded by Moss et al. (2002). Glucose, methanol, glutamic acid and acetone present in two of the synthetic samples are miscible with water. The other five samples in Table 3 contain one or more than one aromatic compound. The hydrophilic nature of glucose, fructose, acetone and methanol on mixing with aromatic compounds shifts towards hydrophilic nature ($K_{OW} < 2$). The shift, however, is independent of the amount of organic compounds.

Another parameter that was discussed in an earlier study was the ratio of K_{OW} to SUVA (Pradhan et al., 2013). It was demonstrated that the ratio of K_{OW} to SUVA ($K_{OW}/SUVA_{\lambda max}$) depends on the functional groups present in the organic compound. For synthetic samples, the $K_{OW}/SUVA_{\lambda max}$ has been found to vary from 6.7 for glucose-fructose-benzene to 135 for benzene-nitrobenzene-KHP. However, the ratio of log K_{OW} to $SUVA_{\lambda max}$ (log $K_{OW}/SUVA_{\lambda max}$) of mixtures containing one or more aromatic compounds is within a narrow range of variation i.e. between 1.0 and 1.5. The slope of the plot between log K_{OW} and $SUVA_{\lambda max}$ (Fig. 2 is 1.13 which, however, is less than the slope of 1.8 obtained for the plot between log K_{OW} and $SUVA_{\lambda max}$ for aromatic compounds by Pradhan et al. (2013). It, therefore, suggests that the behavior of a mixture is dominated by aromatic compounds more than the aliphatic compounds. K_{OW} of aliphatic compounds is less than one or log K_{OW} is negative.

3.2. Organic contaminants in the natural water samples (River Hindon)

The Hindon River from its origin to the confluence is polluted. Water quality characteristics at the sampling locations are pre-

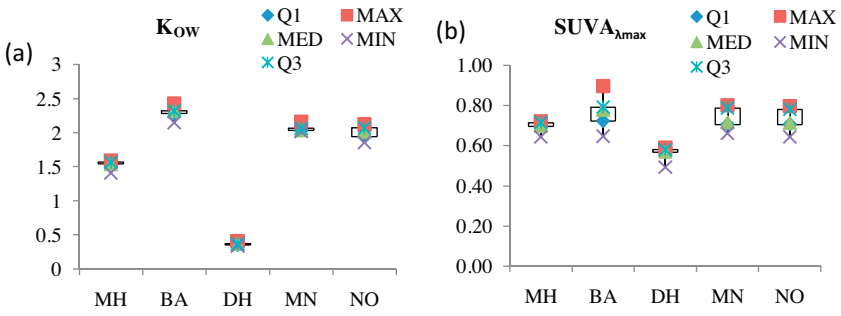

Fig. 3. (a, b). Box plot for K_{OW} and SUVA at five stations of River Hindon.

sented in Tables 4a and b. Results obtained for nine month sample analysis from five sampling locations were verified with statistical analysis of variables (ANOVA). Probability factor ($p < 0.5$) indicates values are considerable. Organic contaminants at four locations namely MH, BA, MN, NO are relatively more than at DH. The discharge of fresh water from the Upper Ganga Canal upstream of DH dilutes and reduces the concentrations of contaminants. DOC of all the samples is ~80% of TOC irrespective of wide range of monthly variations in TOC. The standard error (SE) in normalized water quality parameters is <0.1 (Table 4b). The Total BOD_5 to TOC and soluble BOD_5 to DOC values have been found to vary from 0.4 to 29 and 0 to 7.7 mg/L, respectively. The low ratio 0.13 of soluble BOD_5 to COD indicates the presence of persistent organics in the water (Hermsen and Voortman, 1996). The organic removal, therefore, is not possible via biodegradation. COD is not a measure of organic carbon, but an indication of the oxidative degradation potential of polluted water (Eckenfelder and Grau, 1992). The oxidation state (OS), determined from the molar ratio of COD to TOC was greater than 2. Such compounds are resistant towards oxidation. Values of K_{OW} measured at three different ratios of octanol and water (1:1, 1:2, 2:1) were not significantly different and, therefore, average of these three values has been reported (Table 4b). Values of $\log K_{OW}$ for river Hindon were found to range from −0.46 to 0.37. Average values of $SUVA_{\lambda max}$ and $\log K_{OW}$ of samples from MH, BA, MN and NO were between 0.7 and 0.8 $mg\,m^{-1}\,L^{-1}$ and 0.17 and 0.35, respectively, where as average $SUVA_{\lambda max}$ and $\log K_{OW}$ of samples from DH were 0.57 and −0.43, respectively.

Box plot of K_{OW} and SUVA of water samples from the River Hindon is presented in Fig. 3(a) and (b). It is to be seen that the four stations namely MH, BA, MN, and NO have nearly identical median values of K_{OW} and SUVA. Values at DH are different than the other four stations. Though there is a difference in the nature of organic contaminants in DH sample and other samples, nevertheless, on the basis of log K_{OW} values, all the samples are hydrophilic in nature. Value of log K_{OW} and $SUVA_{\lambda max}$ of the samples from the Hindon river do not match with any of the four categories of compounds reported in authors' earlier study (Pradhan et al., 2013).

This is not surprising, as these samples are the mixture of wide variety of compounds with a wide range of functional groups. Behavior of natural samples is similar to that of synthetic samples. Though these samples contain alcohols, acids etc., the K_{OW} are different than the parent compounds. Each sample has unique K_{OW} and $SUVA_{\lambda max}$, which can help to ascertain hydrophilic and/or hydrophobic nature of the organics.

In order to elucidate the nature of organics, samples were analyzed by GC–MS. Results are presented in Table 5. Of the 14 compounds identified valeric anhydride, a fire retardant is hydrophobic and pyrrolidine, 3-methyl- is moderately hydrophobic. The other 12 compounds are hydrophilic in nature. Among these, 4-aminobenzoic acid (Table 5), which is present in samples from all the locations is a food supplement. The other compounds are agro chemicals, pharmaceuticals, precursors of various synthetic chemicals, personal care products, etc. However, these compounds are reported as toxic. Log K_{OW} of water from BA, MN and NO is around 0.3 is a value between log K_{OW} of 0.19–0.86 for most of the compounds identified by GC–MS. It is to be noted that low value of K_{OW} at DH may be due to 3-mercaptopropane-1, 2-diol ($\log K_{OW}$; −8.4) and 3-amino-2-chloro-pyridine ($\log K_{OW}$; 0.043). These compounds were not found in water from other locations.

4. Conclusion

K_{OW} and SUVA of (i) synthetic samples containing different organics and (ii) water samples from a polluted river were determined. Both SUVA and K_{OW} do not depend on the ratio of organic compounds present in the samples as well as the ratio of octanol to water used for partitioning. These parameters reveal the hydrophilic and/or hydrophobic nature of the sample. Studies on synthetic samples with known composition reveal that the mixture of aliphatic compounds is hydrophilic (log K_{OW} and $SUVA_{\lambda max}$ in $mg^{-1}\,m^{-1}\,L < 0.1$) and mixture of aliphatic and aromatic compounds are also observed as hydrophilic (log K_{OW} and $SUVA_{\lambda max}$ in $mg^{-1}\,m^{-1}$ $L < 0.3$) in nature. Samples that contain aromatic compounds are moderately hydrophobic (log K_{OW} and $SUVA_{\lambda max}$ in $mg^{-1}\,m^{-1}\,L > 1$) and strongly hydrophobic (log K_{OW} and SUVA in $mg^{-1}\,m^{-1}\,L > 2$) in nature. The ratio of $\log K_{OW}$ to SUVA shows a narrow range of variation. However, ratio of K_{OW} to SUVA is sensitive to the nature of organics. The values of log $K_{OW} < 0.4$ and SUVA in $mg^{-1}\,m^{-1}\,L < 0.8$ of Hindon water samples shows hydrophilic in nature. The identification of compounds by GC–MS further corroborates hydrophilic nature of the Hindon water samples. The outcome of this study can be used to estimate residence time for the purification of polluted water containing the mixture of organics. Various authors have reported good correlation between log K_{OW} and adsorption parameters for single organics. It can be extended to natural samples containing several organics that vary widely in nature. Sorption experiments on the mixture of organics are in progress.

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